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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
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BROMINE AND IODINE

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PAUL M. TYLER AND AMY B. CLINTON

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November, 1930

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

BROMINE AND IODINE[1]

By Paul M. Tyler[2] and Amy B. Clinton[3]

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6387."

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FOREWORD

The four elements fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) form the most intimate family in the entire system of elements and are grouped under the name "halogens" or salt formers (by derivation from the Greek). The first member of this family, fluorine, is the most chemically active element known; and fluorspar, and to a less extent cryolite, the chief sources of fluorine, are important commercial minerals. Fluorine occurs in nature chiefly in combination with sodium as common salt, but it also appears in other natural compounds in sea water, salt-well brines, and bedded deposits. In addition to common salt, various compounds containing chlorine (chlorides) have long been consumed by industry on a large scale, and within the last two decades that element itself has come rapidly into prominence as one of the leading industrial chemicals. Bromine and iodine, the two retaining members of the family, are less abundant in nature and less readily isolated and in consequence of their relatively high price have found few industrial uses, being consumed chiefly in medicine and in photography. Bromine, however, is now entering the industrial field to a considerable extent, due to the rapidly growing use of ethylene dibromide in anti-knock compounds for gasoline.

The present paper is devoted to bromine and iodine, but in order to comprehend the physical and chemical characteristics of these two elements (and hence their potential economic significance) it is convenient to consider them as members of the family series to which they belong. The family relationship of the halogens is illustrated by the following:[4]

(1) The similarity in the chemical and physical properties of the elements and their corresponding compounds is such that the properties of any one member of the family can be said to summarize or rather to typify the properties of all the other members, although fluorine diverges a little in some of its properties.

(2) The gradual transition of chemical and physical properties is such that if the elements are arranged in order - F, Cl, Br, I - the variation in any particular property in passing from fluorine to iodine nearly always proceeds in the same order, and that is the order of their atomic weight. Taking almost any property and comparing its magnitude in passing from the element fluorine to iodine, or from the fluorides to the iodides, a similar gradation will be observed. Thus, take the melting point of the cadmium, calcium, barium, sodium, or potassium salts, in degrees.

	Fluoride	Chloride	Bromide	Iodide
Sodium	980	820	765	650
Potassium	885	790	750	705
Calcium	1361	780	760	740
Barium	1280	960	880	740
Cadmium	1000	590	350	1000

The markedly greater jump in passing from the fluorides to chlorides than with the other steps in the case of the earths is supposed to be explained by a difference in constitution. There is also a difficulty with the cadmium halides, but these exceptions serve only to emphasize the general rule.

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[4] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry; London, vol. 2, 1922, pp. 66-67.

Table 1.- Physical Properties of the Halogens

	Fluorine	Chlorine	Bromine	Iodine
At. wt.	19.0	35.46	79.92	126.92
State aggregation (0°).	Gas	Gas	Liquid	Solid
Color	Pale yellow	Yellowish-green	Brownish-red	Violet
Sp.gr. (liq.)	1.108 (-187°)	1.568 (-33.6°)	2.9283 (59°)	4.004 (107°)
Sp.vol.	.9025	.6635	.3392	.2698
At. vol.	17.15	23.52	27.13	34.23
Mol. vol.	34.30	47.04	54.26	68.46
B.p.	-187°	-33.6°	50°	183°
M.p.	-233°	-102°	-7.3°	114°
Critical temp.	- -	147°	302°	512°
Coeff. expansion	- -	.00187 (0°)	.00106 (0°)	.000025 (liq)
Coeff. compressibility.	- -	.00095	.000052	.000013
Heat of fusion	- -	22.96 cals.	16.185 cals.	2.9 cals.
Heat of vaporization ..	- -	67.38 cals.	45.6 cals.	81 cals.
Sp. ht. (0°)	- -	.2662 (liq.)	.1071 (liq)	.0515 (solid)
Sp. ht. gas, C_p	- -	.1155	.0553	.0336
Sp. ht. gas, C_v	- -	.0873	.0428	.0257
Ratio y	- -	1.323	1.292	1.307
Refractive index	1.000195	1.000768	1.001125	1.001920
At. dispersion	.022- .05	.50	1.22	3.65
At. refraction	.941-1.015	10.05	15.3	24.5
Magnet, susceptibility.	-3.45×10^{-6}	5.9×10^{-6}	-4.1×10^{-6}	-3.5×10^{-6}
Dielectric constant ...	- -	1.97	3.18	4.00

BROMINE

General Description

Bromine is a dark reddish-brown, highly corrosive liquid which volatilizes easily, giving off heavy vapors. If inhaled the vapors are suffocating and cause great irritation of the air passages. The liquid attacks the skin and causes sores that heal very slowly. Owing to the corrosive nature of the element it enters commerce largely in the form of its salts, of which sodium bromide, potassium bromide, and ammonium bromide are listed in the United States Pharmacopoeia (which specifies that they must be 98.5 per cent pure). Ethyl bromide or hydrobromic ether is a colorless, inflammable liquid possessing a sweet taste with a burning aftereffect; it may be prepared by distilling absolute alcohol with bromine (and then purifying with potassium hydroxide and again distilling). Ethylene bromide or dibromoethane, also a colorless liquid, is volatile, emulsifiable, and poisonous; its odor resembles that of chloroform and it is prepared by the action of bromine on ethylene gas. Bromine is also sold as "mining salt," a mixture of sodium bromate and bromide. Solidified bromine has been used for laboratory work. Diatomaceous earth, formed with a suitable binder and burned into coherent sticks, is saturated with the liquid. These porous sticks absorb 50 to 75 per cent of bromine by weight.

Uses

Previous to about 1922 bromine was used principally in the form of sodium potassium or ammonium bromide in photography and for medicinal purposes. The photographic trade usually buys ammonium bromide of U. S. P. grade (containing not less than 98.5 per cent ammonium bromide when dried for 24 hours over sulphuric acid). "Mining salt" was formerly used in some quantity in the extraction of gold from its ores, but this use has apparently greatly declined. Bromine is used in the production of certain dyes, and liquid bromine as well as many of its compounds is employed in analytical chemistry. During the War some hand grenades and gas bombs were loaded with bromine or with organic bromine compounds.

The principal outlet for bromine at present, however, is as ethylene dibromide used in tetraethyl lead, antiknock compounds.

Occurrence and Sources of Supply

Bromine does not occur uncombined in nature, but in the form of bromides, usually accompanying common salt and magnesium chlorides, it is widely distributed. The chief, if not the sole, commercial source of bromine in the United States has been the bromides recovered from salt brines. Bromine is found in sea water, in a large number of mineral waters and salt springs in different parts of the world, and in a number of brine wells in Michigan, Ohio, Pennsylvania, and West Virginia. The greater part of the bromine produced in the world comes from the deposits of potash salts in the Stassfurt region of Germany, the various brines of the United States furnishing practically all the remainder. The element is also found in small amounts in some French phosphates, and in Silesian zinc ores.

Until a few years ago the supply of bromine from Chile, Germany, and the various salt wells in the United States apparently far exceeded any probable demand, but as bromine began to be used in rapidly increasing quantities in motor fuel attention was drawn to the bromine content of the sea. Bromine occurs in sea water to the extent of 60 to 70 parts per million, except of course where fresh water from rivers may cause local dilution near the coast. Since the area of the oceans is 139,295,000 square miles--almost two and one-half times the area of the land--and since the depth averages 3 miles, sea water represents a virtually inexhaustable source of supply of any chemicals that can be commercially extracted therefrom. The cruise of the S. S. Ethyl demonstrated that this bromine actually is available, and the importance of this discovery is evidenced by the fact that only 1 cubic mile of sea water would supply for 392 years all the requirements of a plant producing 100,000 pounds of bromine per month.

In addition to the various occurrences in a dissolved condition, bromine is a constituent of two silver ore minerals, bromyrite ($AgBr$) and embolyte ($Ag(Cl\ Br)$); but these are quite rare.

History

The elemental nature of bromine and its relation to chlorine and iodine were apparently discovered by A. J. Balard about 1824. At first he called the substance "muride" but afterwards named it bromine from a Greek word meaning a stench. Balard published an account of his work in his Memoire sur une substance particuliere contenue dans l'eau de la mer (Ann. Chim. Phys. vol. 32, 1826, p. 337).[5]

A most interesting chapter in the history of bromine relates to the cruise of the S.S. Ethyl. To investigate the feasibility of the recovery of bromine from seawater, the Dupont Co. and the Ethyl Gasoline Corporation purchased the Lake Harmonia, an oil-burning steel cargo steamer of the lake type (253 feet 8 inches long, 43 feet 8 inches beam, 4,200 tons dead weight). This vessel, after being converted into a floating chemical plant and renamed, finally put out to sea about the first of May, 1924. It was equipped to handle 7,000 gallons of water a minute carrying 4 to 5 pounds of bromine. Tests made in various parts of the ocean demonstrated the feasibility of recovering bromine commercially from this source.

Methods of Extraction

Bromine is produced from natural and artificial brines and may be removed from the concentrated bitterns remaining after the sodium chloride has been recovered or by direct treatment of the unconcentrated brine before the salt is removed.

Three distinct methods have been employed commercially, namely (1) a batch process using sulphuric acid and an oxidizing agent; (2) a continuous process involving treatment with chlorine gas; and (3) another continuous process in which an electric current instead of chlorine is employed to liberate the bromine.

In the first-mentioned process the bitterns after the salt has been removed are concentrated further and then treated in a sandstone or chemical stoneware still with a calculated quantity of sulphuric acid and sodium chlorate (or other oxidizing agent such as manganese dioxide). A steam jet passed into the solution assists in eliminating the bromine in the form of a gas which passes out of the still. Impurities, chiefly chlorine, are removed by washing the gas with milk of lime, after which the bromine is condensed.

In the chlorine process air is employed to remove the liberated bromine from the solution, and the resulting mixture of air and bromine is passed over scrap iron or iron filings, forming iron bromide. Sufficient moisture is present to dissolve this compound, and the concentrated solution of iron bromide so obtained is treated with more chlorine. This once more liberates the bromine which (being only slightly soluble in the iron-chloride solution which is simultaneously formed) settles to the bottom of the chamber and can be withdrawn.

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[5] Mellor, J. W., Work cited, p. 24.

The electrolytic process depends upon the principle that bromides can be decomposed at a lower temperature than chlorides, which consequently need not first to be removed. The liberated bromine is carried out of the brine by means of air and purified, as in the second process described above.

The continuous processes have been covered by numerous patents; and for some time the Dow Chemical Co., the largest producer of bromine in the United States, had a practical monopoly of their use, but this condition no longer exists[6]

World Production

The world's bromine has come chiefly from Germany and the United States. Bromine was produced in the United States as early as 1846; but prior to 1860 very little bromine was made as it was used only for scientific purposes. As a greater demand arose in the fields of medicine and photography the practical recovery of bromine began in 1865 from the Stassfurt deposits, with the production of less than 2,000 pounds. About 1867, bromine began to be made in the United States along the Ohio River (Pomeroy district) as a by-product of salt manufacture. Between 1904 and 1908 a price war developed between Germany and the United States; and as a result of large stocks accumulated at low prices during this period, the domestic production of bromine, which had been built up to over a million pounds annually, dropped to 250,000 pounds in 1910. After increasing to 651,541 pounds in 1911, it declined again to 572,400 pounds in 1913. In Germany the output reached 2,061,301 pounds in 1908. In 1912, it amounted to 1,909,184 pounds.

From these figures it would appear that the demand for bromine was less than 1,500 tons annually in the years immediately preceding the outbreak of the World War. The immediate effect of the war was largely to increase the demand for bromine, both in the manufacture of war gases and for medicinal purposes. During this period the United States supplied England and France, as well as this country, and the plants along the Ohio River which had been closed because of German competition were reopened. Production increased rather slowly at first, but by 1918 almost 1,727,156 pounds of bromine were recovered in the United States, chiefly in the form of sodium bromide. After 1919 there was some decrease in production, but since 1923, due to the increasing use of bromine as an addition to gasoline, the production in the United States increased first to 2,000,000 pounds and finally in 1929 jumped to 6,414,620. No figures are available as to total world production in recent years; but it is known that the industry in Germany has also grown (producing 1,800 tons in 1929), and in addition bromine is being or is likely to be produced in other foreign countries, including France, Italy, Russia, and Palestine.

Domestic Production

The production of bromine from the bitterns left after salt production has been carried on in the United States, principally in Michigan, Ohio, and West Virginia. The districts producing bromine have been the following:

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[6] Dow Chemical Co. v. America Bromine Co. and Arthur E. Schaefer, 210 Mich. Sup. Ct. Rep., 262.

In Michigan, Saginaw and Charles in Saginaw County; Bay City in Bay County; Midland in Midland County; and Mount Pleasant in Isabella County. At Midland and Mount Pleasant the bulk of the bromine produced is sold as bromides of potassium, sodium; and ammonium. Operations at Midland are under the control of the Dow Chemical Co., the largest operator.

In the Ohio Valley bromine-production centers are at Pomeroy, Meigs County, Ohio, and on the opposite side of the river at Mason and Hartford, Mason County, W. Va.

Another bromine production center is at Malden, on the Kanawha River, Kanawha County, also in West Virginia.

In 1924 there was a great increase of production of bromine in the United States, the output in that year amounting to 141 per cent of that of 1923, owing to the sudden demand for the production of tetraethyl lead. In 1925 there was a decline in production of 23 per cent compared with 1924, on account of the temporary restriction by the authorities of the production of tetraethyl lead, but as this difficulty was soon disposed of production has subsequently continued to rise rapidly.

In 1928 the bromine recovered by the producers from natural brine and the bromine content of bitterns used by producers in the manufacture of bromine compounds was 23 per cent more than in 1927. The larger part of the bromine output as reported is not sold as bromine but as potassium and sodium bromine and other salts. The plants operated in 1928 were those of the California Chemical Corporation, 233 Sansome St., San Francisco, Chula Vista, Calif.; the Dow Chemical Co., Midland, Mich.; Pomeroy Salt Corporation, Pomeroy, Ohio, Minersville, Ohio; The Excelsior Salt Works, Pomeroy, Ohio; J. Q. Dickinson & Co., Malden, W. Va.; Liverpool Salt & Coal Co., Hartford, W. Va.; and Westvaco Chlorine Products, Inc., South Charleston, W. Va. In 1929 the bromine recovered by the producers from natural brine and the bromine content of bitterns used by producers in the manufacture of bromine compounds was 6,414,620 pounds. This is nearly three times as much as the output for 1928, which was 2,164,000 pounds. This increase was due in most part to bromine required for ethylene dibromide used in the manufacture of ethyl gasoline.

Marketed Production of Bromine in the United States[1]

		Value				Value	
Year	Quantity	Total	Per lb.	Year	Quantity	Total	Per lb.
	Pounds				Pounds		
1913	572,400	$ 115,436	$0.20	1921	711,953	172,759	$0.24
1914	576,991	203,094	.35	1922	1,005,174	150,668	.15
1915	855,857	856,307	1.00	1923	842,352	146,176	.17
1916	728,520	951,932	1.31	1924	2,033,804	594,685	.29
1917	895,499	492,703	.55	1925	1,566,130	488,406	.31
1918	1,727,156	970,099	.56	1926	1,245,760	426,837	.34
1919	1,854,971	1,234,969	.67	1927	1,759,000	564,760	.32
1920	1,160,584	745,381	.64	1928	2,164,000	649,475	.30
				1929	6,414,620		

[1] Includes bromine content of potassium and sodium bromides.
Data compiled by A. T. Coons, U. S. Bureau of Mines.

Imports

Imports of bromine were a serious factor in the domestic industry in the late eighties, early in the nineties, and again between 1904 and 1908, but subsequently they became very small. Since 1923, however, they have shown some tendency to increase, and for several years the imports of sodium and potassium bromides and of other bromine compounds from Germany have supplied a substantial part of the domestic consumption. The imports of bromine compounds were not separately recorded, however, before 1922. The bulk of the imports under the classification "bromine compounds n.s.p.f." consist of ethylene dibromide. Import statistics follow:

Year	Bromine		Potassium bromide		Sodium bromide		Bromine compounds n.s.p.f.	
	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
	Pounds		Pounds		Pounds		Pounds	
1922 Sept. 22 Dec. 31	644	$ 206	11,717	$ 973	61,736	$ 5,414	- - -	- - -
1923	782	1,171	52,833	5,736	114,341	10,574	4,123	$ 1,581
1924	37,318	8,958	935,749	124,414	713,659	110,215	52,408	13,071
1925	8,009	2,110	237,231	62,028	208,434	52,230	117,867	46,764
1926	37,839	14,486	70,440	18,549	212,365	73,313	271,645	102,894
1927	- - -	- - -	20,813	7,075	1,102	370	465,048	144,167
1928	- - -	- - -	23,231	7,918	- - -	- - -	310,935	89,823
1929	17,573	5,804	28,310	9,834	110	51	643	522

Tariff Duties

After being on the free list in the Act of 1913 bromine was made dutiable at 10 cents a pound under the Act of 1922, which provided the same duty on "all bromine compounds not specially provided for" (par. 46) and on potassium bromide (par. 80) and sodium bromide (par. 83). The duty of 10 cents a pound was retained in the Act of 1930 (par. 45, 78, and 81, respectively).

Germany

Before 1914 Germany was the largest producer of bromine and its compounds. The crude potash material (carnallite) at Stassfurt contains 0.15 to 0.25 per cent of bromine. Only part of the waste liquors left after the removal of potash is utilized in the manufacture of bromine, and hence the figures of actual production give little indication as to Germany's capacity to produce the element. In 1912 the output was 1,909,184 pounds of bromine, of which 1,254,017 pounds were used in the manufacture of bromine and its compounds and 564,378 pounds in the manufacture of dyes. Exports apparently accounted for as much as 60 per cent of the prewar production, amounting in 1913 to 1,150,000 pounds of bromine (equivalent).[7]

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[7] U. S. Tariff Commission, Information Survey: FL-8, 1921, p. 22.

Previous to the World War German manufacturers of bromine were united in a cartel known as the "Deutsche Bromkonvention" organized as a limited liability corporation (G. m. b. H.) with headquarters at Stassfurt-Leopoldshall. In 1930 four new syndicates covering by-products of potash production were reconstituted under a covering trust, I. G. der deutschen Kaliindustrie G. m. b. H., thereby establishing a uniform sales policy (with production quota allocations) with respect to bromine, rock salt, magnesium chloride, and magnesium sulphate, respectively. A later contract prolonged the four syndicates from June 30, 1930 to June 30, 1935.[8]

In 1929 the production of bromine in Germany was 1,800 metric tons; and the exports were 233 metric tons, which compares with 184 tons exported in 1928.

Other Foreign Countries

Australia.- The Cheetham Salt Proprietary, Ltd., of Geelong, Victoria, engaged in the manufacture of salt from sea-water, produces a mother liquor having a density of 36° B. and containing 0.47 per cent of magnesium bromide. In an average year 23 tons of magnesium bromide would be available. This amount could be doubled when the present works are fully developed.

France.- Bromine is extracted from the concentrated Alsatian potash liquors by at least two plants in France, and the output from the source increased to 230 metric tons in 1928 and might be almost doubled.[9] Since the Societie d'Alais, Froges, et Camargue can produce an additional 120 tons, the total potential supply is in excess of 500 metric tons annually. Domestic consumption is around 200 tons a year so that the exportable surplus may be as much as 300 tons. Actual exports were 167 tons in 1928 and 110 tons in 1927. There were no imports of bromine in these years.

India.- A salt industry has been carried on under Government control in the Rann of Cutch, India, at Kharaghoda, from 1887 up to the present time, and also for some time at Dhrangadra, where there are a number of brine wells. The brines are treated by solar evaporation for the production of common salt. They contain, besides, a considerable proportion of magnesium chloride and a notable amount of magnesium bromide; but, unlike sea water, they contain no potash salts.

Italy.- Extraction of bromine in Italy was started in 1928 by the Societa Italiana del Broma of Rome. The bromine is recovered from the concentrated liquors of one of the largest salt lakes in Italy. The initial daily production was 80 to 100 kilos, to be increased to 130 to 150 kilos.

Palestine.- Bromine is a potential by-product of the extraction of potash under the Dead Sea project. The River Jordan is unusually rich in the chloride of sodium as well as chloride of magnesium, but in the Dead Sea as a result of continued evaporation a large proportion of the sodium chloride is precipitated, whereas a preponderant amount of magnesium chloride, together with potassium chloride, together with potassium chloride, magnesium bromide, and other salts is left in solution. The waters of the lake, in short, are natural bitterns. On the basis of the estimated production of 100,000 tons of muriate of potash, mother liquors containing about 50,000 tons of magnesium bromide (and about 1,000,000 tons of magnesium chloride) would be returned to the sea. Preliminary investigations, however, indicate that so long as the market for bromine is relatively small and irregular that particular material could probably be supplied adequately from other sources and would not pay to attempt to recover.

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[8] Daugherty, W. T., World Trade Notes: U. S. Bureau of Foreign and Dom. Commerce, vol. 4, No. 8, Feb. 24, 1930, p. 2.

[9] Chimie et Industrie, L'Industrie Chimique Francais in 1928 - Le Brome. vol. 21, No. 5, May, 1929, p. 1083.

Russia.- Work has been done on industrial processes for the extraction of magnesium, bromine, and iodine from the inexhaustible supplies of these materials in the salt waters of various seas in Russia.[10] Until recently these sources have been only incompletely tapped, but in 1923 two magnesium chloride works were established, one in the Crimea and the other at Odessa. The amount of bromine that may become available from such operations is very large. Although consideration has been given methods of recovering the bromine no data as to actual production are available. It was stated, however, that factory on Saksky Lake, not far from Eupatoria, Crimea, was expected to produce at least 30 tons of bromine a year.[11]

United Kingdom.- Although the salt industry has been carried on for a long period and over a large area in England, it has been very rare for minor constituents, such as bromine, iodine, or potash, to be given in the numerous analyses that have been published. During the World War an inquiry was made into the possibility of obtaining bromine from brine, and various brines from Cheshire and Stafford were found to have bromine contents from 0.005 to 0.008 gram per 100 cubic centimeters. Brine from the Point of Ayre salt field, Isle of Man, has been found to contain 0.16 per cent of bromine.

According to information supplied by G. W. Malcolm, of the Salt Union, Ltd., that company pumps 500 million gallons of raw brine per year for salt manufacture. This brine has a bromine content of 0.08 gram of bromine per liter, which corresponds to a total bromine content of 180 tons. The operations of the company are, however, carried on over a scattered area, and under present conditions of production the recovery of the bromine is regarded as commercially impracticable.

Markets and Prices

The recovery of bromine from the Stassfurt deposits, begun in 1865, brought the price down from $10 to $4.50 a pound and during the next few years the price declined further to $1.30. According to Thorpe[12] the price, due to the ability of Americans at that time to undersell the Germans, had dropped in 1885 to below 7 cents a pound (0.70 mark per kilogram) in Germany. In the United States, however, the price in that year dropped only to 25 cents and soon advanced above 30 cents, reaching 35 cents in the following year.[13] The National Bromine Co. formed about that time did much to stabilize the industry, establishing a regular market and standardizing methods for transporting this dangerous material. This company, virtually a sales agency for the principal producers, expired in March, 1891. Agreements with German producers as to sales territories being thus automatically ended, imports, apparently nonexistent since 1887, were resumed, and as American producers likewise attempted to dispose of their stocks the price slumped from 25 cents to 17½ cents a pound at New York. or say 16½ cents at producing localities in West Virginia and Michigan. As bromine itself was difficult to import the Germans made it up into bromides of potash or soda, and these compounds also dropped in price, potassium bromide falling to 21 cents a pound.[14] By 1893 a better understanding was reached between American producers and prices returned to about 25 cents.

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[10] Panteleimonov, B. G. The question of utilization of salt sea solutions. Chem. Ztg. vol. 54, pp. 153-155, Feb. 22, 1930.

[11] Oil and Color Trades J., London, Russian Bromine, vol. 70, No. 1459, Oct. 2, 1926, p. 1131.

[12] Thorpe, Edward, Dictionary of Applied Chemistry, (1921 ed.): London, vol. 1, p. 689.

[13] Min. Res. of the U. S., 1886, U. S. Geol. Survey, Bromine, pp. 642-643.

After an uneventful decade, during which prices ranged from 26 to 30 cents, production began in 1904 to increase rapidly, and the combination of overproduction and increased imports from Germany carried the price down from 30 cents in 1904 to 20 cents in 1907. Domestic production, which had reached a maximum of 1,379,496 pounds in 1907, was drastically reduced, amounting in 1910 to only 245,437 pounds, the smallest output since 1887; and as imports from Germany ceased in 1910, the industry began slowly to come back to normal.

In 1913 the wholesale price of bulk bromine in New York ranged from 25 to 35 cents a pound. The outbreak of the World War cut off German photographic and other bromine chemicals, and as the demand for American bromides increased the price rose much faster. The peak of $6.50 a pound was reached in 1916. This high price, of course, was largely artificial, but the average price of the domestic production as reported by producers was $1.31 a pound, the highest since 1865. Quotations dropped rapidly in 1916, and by the end of the year reached $1.30. By the middle of 1917 they were down to 55 to 60 cents, and the prices reported by producers likewise declined, the average for 1917 being 55 cents. In that year the new Brombenzyl cyanide, a tear gas for use in the trenches, was invented and thenceforth demand kept step with supply despite the new production obtained from brine wells drilled in the Midland district in 1918 under Government stimulation. Following the Armistice there was a brief decline in price, but as the demand for bromide increased in the photographic trade, especially for moving picture films, and also for the treatment of nervous diseases, the quotations in 1919 reached 75 to 85 cents, while the average price realized by producers increased to 67 cents. The 1921 depression resulted in a new low average price of 15 cents per pound in 1922, but in 1924 the average receipts on domestic sales rose to 29 cents. In 1929 the figure was 30 cents.

New York quotations since 1926 have remained at 45 to 47 cents (bromine, purified, in casks). Other bromine products were quoted in New York, July, 1930, as follows:[15]

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[14] Mineral Resources of the U. S., U. S. Geol. Survey, Bromine, 1891, p. 579.

[15] Oil, Paint, and Drug Reporter. Current Market Quotations. Vol. 118, No. 2, July 14, 1930, p. 5.

	Cents per pound
Ammonium bromide, granular, barrels	48 - 49
Sodium bromide, barrels	42 - 43
Potassium bromide, barrels	42 - 43
Bromoform, U.S.P., jars	180 -190
Ethyl bromide, pure, bottles	85 - 95
Ethyl bromide, technical, drums	50 - 55
Ethylene dibromide, drums	70

In 1928 bromine was quoted in Germany at the equivalent of 30.25 cents a pound for home consumption. Potassium bromide ranged from 29.2 to 31.3 cents and sodium bromide from 31.3 to 33.0 cents a pound; export prices were a fraction of a cent a pound higher.

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IODINE

Description

Iodine is a gray or purple black, crystalline solid, somewhat metallic in appearance, which volatilizes easily and gives off a violet vapor. Even at ordinary temperatures it volatilizes spontaneously in the air, diffusing an odor similar to that of chlorine. The vapor is one of the heaviest known gases, having a specific gravity of 8.801.[16] The characteristic color of this vapor gave the element its name, which is derived from the Greek word for "violet." The element is very sparingly soluble in water but readily forms violet solutions in chloroform, bromoform, carbon disulphide, kerosene, and benzene. In alcohols (ethyl, methyl, and amyl) and also in ether and glycerol it forms brown solutions. It is very soluble in potassium iodide, due to the formation of a compound, KI_3. In chemical affinity it resembles other members of the halogen group; but being less energetic than fluorine, chlorine, or even bromine it may be displaced from its compounds by these elements.

The characteristic reaction of free iodine is the formation of a dark-blue compound with starch.

Uses

Iodine is used largely in medicine in the form of its salts, many of which are official in the United States Pharmacopoeia. By far the most important is potassium iodide; others include sodium iodide, ammonium iodide, arsenious iodide, mercuric iodide, iron iodide, and strontium iodide.

A rough estimate of the uses of crude iodine is as follows: Potassium iodide, 75 per cent; sodium iodide, 7½ per cent; resublimed iodine, 7½ per cent; all other compounds, 10 per cent.[17]

Potassium iodide is obtained in white, colorless crystals and is used in medicine and in sensitizing solutions for photographic films; it is also an important reagent in chemical laboratories. Sodium and ammonium iodides have the same uses as potassium iodide, but the former does not crystallize as well as the potassium salt and hence is not so readily purified; ammonium iodide is used principally in photography. The other compounds are used in medicine.

The lack of iodine in the human system is said to cause goiter, and in some localities the municipal authorities cause iodine to be dissolved in the drinking water supply from public works. Iodine is also added to table salt as a corrective or preventive of thyroid diseases. In alcoholic solutions iodine is a well-known antiseptic, and the element is often sprinkled about hospitals as a disinfectant.

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[16] Thorpe, Edward, Work cited, p. 640.

[17] U. S. Tariff Commission, Tariff Information Survey, A-9: 1921, p. 102.

In analytical chemistry iodine is invaluable. Its use in oil analysis for the so-called "iodine value" has greatly facilitated the examination of oil samples, and its use in the titration of reducing agents (iodimetry) has been ingeniously adapted to the estimation of almost every known substance.

As a fertilizer, the addition of an iodide to certain soils is said to result in substantially greater yields of crops.[18] Because of its iodine content Chilean nitrate of soda is claimed to be a more effective fertilizer than is the purified nitrate of soda of the laboratory. Iodine is also said to be used as an ingredient in certain dyes and paints.

Occurrence and Sources of Supply

Iodine in minute quantities is quite widely distributed throughout the animal, vegetable and mineral kingdoms. As a mineral it occurs in combination with silver, mercury, and lead, in ores from Mexico, Chile, and Spain, with zinc in Silesia; and with lead in South America. Iodine is always present in sea water, but the percentage is so small that it is difficult even to detect its presence. All fishes and all animal products from the sea, as well as seaweeds or marine algae, likewise appear to contain iodine but usually in very minute quantity.

Iodine seldom occurs free in nature, although minute traces are found in certain mineral waters, notably those of Bath, Cheltenham, Harrogate, and Woodhall in England, and those of Heilbronn, Vichy, Carlsbad, and Marienbad on the continent.

The two principal commercial sources of iodine, the sea and nitrate deposits, both contain iodine in combined form.

The bulk of the iodine supply of the world comes as a by-product from the working of the Chilean nitrate deposits, although some iodine is still extracted from seaweed in Scotland, France, and Japan, and also in Norway.

Still a third source is indicated by developments in Italy, where iodine is derived from the mother liquors of the salso-bromo-iodic mineral water of Salsomaggiore and in Java, where it is found in the form of iodate in the waters of springs and artesian wells.

In the United States and also in parts of Russia iodine is found in oil well waters in recoverable amounts.

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[18] Firman, E. Bear, Medicated Fertilizers: Am. Fert., vol. 68, April 20, 1927, pp. 23-5.

The concentration of iodine in sea water is so extremely small that direct extraction would be commercially impossible, but certain seaweeds are able selectively to absorb the iodine within their cell structure and by burning such weeds an ash comparatively rich in iodine may be obtained. The amount of iodine in seaweed is subject to wide variation. Some varieties contain more than others, and there is a distinct tendency to seasonal variation as well as regional differences in the iodine content of similar varieties of the weed. Ordinarily September is the best month in which to harvest, but the iodine content is always small, usually being less than one-third of 1 per cent, even of the dry weed. By careful burning a good grade of drift weed should yield an ash or kelp containing 25 to 30 pounds of iodine per ton, but 12 pounds is probably above the average actual recovery in many localities.

In the Chilean nitrate deposits the iodine occurs in the form of iodates, which accumulate in the mother liquors from the purification of the nitrate. In the higher-grade material (caliche) the amount of iodine averages 0.15 per cent, while in the low-grade material (costra) the amount of iodine averages 0.05 per cent. The small amount of iodine present makes it obvious that the recovery of this element can only be carried on as a subsidiary by-product industry. The amount of iodine which can be conveniently extracted from the raw material is only about 15 to 20 per cent of the whole quantity available, since during the purification of the crude nitrate only a small part of the calcium iodate is converted to the soluble sodium iodate.

In Germany iodine has been found in coal. Ernst Wilke-Dorfurt and Hermann Romersperger[19] by means of new analytical methods, have found an average of 6 mg. of iodine in 1 kg. of coal; coal from Saxony was richest containing 11.17 mg. per kg.; and Bohemia came next in order, containing 10.21 mg. per kg. The poorest coal examined was Silesian brown coal, which contained but 0.85 mg. It is difficult to imagine in what manner this iodine may be economically recovered, but the iodine content of coal may have an important biological influence. Assuming that 1,200 million tons of coal are burned annually, then some 7,200 tons of iodine are mobilized each year and returned to the cycle of materials at the earth's surface. It is estimated that probably five-sixths of this quantity enters the atmosphere upon utilization of the coal and is taken up by plants and animals.

History[20]

Iodine was recognized as an element before bromine. It was discovered in 1812 by Courtois in the mother liquors of kelp. The discovery was announced to the French Institute in 1813. Clement, Desormes, Gay-Lussac, and Davy all assisted in investigating the properties of the new element.

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[19] Roth, Walter, Coal is found rich in iodine: Ztschr. anorg. allgem. Chem., vol. 186, 1929, p. 159.

[20] Data mainly from Edward Thorpe's Dictionary of Applied Chemistry, London, vol. III, 1922, p. 640.

Courtois, a saltpetre maker in Paris, used the calcium extract as a source of potash salts to decompose calcium nitrate obtained from niter beds which at that time were worked in various parts of France. The original discoverer failed to make a commercial success of his enterprise, but afterward MM. Cournerie of Cherbourg were responsible for establishing the manufacture of iodine on the Normandy coasts, where it became an important industry. In Great Britain iodine was first produced in quantity at Glasgow in 1841. The imports of kelp into the Clyde in that year amounted to 2,565 tons. In 1845 there were four small works engaged in the manufacture of iodine. Kelp was then used for soap making, on account of the sodium carbonate it contained, and the iodine was extracted from the lyes of the kelp boilers. In the following year there were 20 makers of iodine in Glasgow, who then treated the kelp directly, extracting also the potash salts, which had a high value in the market. Following the discovery of the Stassfurt deposits the price of potash salts dropped to one-third of the former price, and due to the variable character of the kelp used and the extreme fluctuations in the price of iodine (ranging from 4 to 34s. per pound) the number of makers was soon reduced to only three or four.

For many years kelp constituted the only commercial source of iodine; but in 1874 iodine began to come into Europe in quantity from Chile, where it is produced as a by-product of the sodium nitrate industry. That country has long remained the principal source of the element.

Kelp[21]

The name kelp, originally applied to the ash obtained by burning seaweed, has been extended to include the seaweed itself, particularly the varieties yielding potash, iodine, and other valuable products. Drift kelp is the only variety now employed as a source of iodine. It is made from the red wracks, Laminaria digitata (or tangle) and Laminaria stenophylla, which are always submerged by the tide, and which contain about 10 times as much iodine as the black wracks or fuci (Fucus vesiculosus, Ascophyllum nodosum, and F. serratus), which are all uncovered at low tide and which are known as "cut weed."

The history of kelp or varec, as it is called in France, is extremely interesting. It is a crude, rough slag made by burning seaweed in long, shallow pits. For many years it was an important and valuable article of commerce and a source of great profit to the proprietors of estates in the West Highlands of Scotland, where it was principally made. At the beginning of the last century it was worth £20 to £22 a ton, and the Hebrides alone yielded some 20,000 tons, worth more than £400,000 annually. It was then the only source of soda and was used largely in soap making and in glass manufacture. The importation of "barilla,"[22] a somewhat similar product obtained by burning various species of land or marine plants, gave the first blow to kelp which consequently fell in price, averaging £10 10s. a ton for the 22 years ending 1822. The duty was then taken off barilla, the price of kelp again fell to £8 10s., and as a result of the repeal of the salt duty in 1823 kelp fell to £3 and then in 1831 to £2 a ton, which price made it unprofitable to manufacture. Meanwhile, soda was being made more and more by the Leblanc process, and kelp was soon superseded altogether as a source of soda. Since it yielded a maximum of about 4 per cent of alkali and often less than 1 per cent, kelp was never a cheap source of soda.

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[21] Data mainly from Edward Thorpe's Dictionary of Applied Chemistry, London, vol. III, 1922, pp. 641-643.

[22] This word should not be confused with the Bolivian, "barrilla," or tin concentrate.

As the manufacture of iodine and potash salts began to assume some importance a new demand for kelp began to appear but it called for a different kind of kelp. The seaweed hitherto employed by the kelpers was of a kind containing little iodine and not very rich in potash. The black wrack or fuci cut in large quantities in the highlands at low tide no longer could be utilized, and the laminaria or drift-weed varieties are the only ones now employed. These weeks are torn up by storms from the rocks on which they grow and cast ashore.

Potassium chloride was at first an important by-product of this new seaweed industry, but when the price of potash was reduced as a result of the discovery of the Stassfurt deposits the profit from the operation was much reduced. Since the Stassfurt mineral also contained bromine and since the price of bromine also declined tremendously (from 33s. to 1s.3d. per pound), still another source of profit was eliminated. The amount of bromine in kelp is small, only about one-tenth that of the iodine, and hence it has not been extracted from this source for many decades. Bromine is much more abundant than iodine in sea water, but the algae select the iodine in preference to the bromine.

Methods of Extraction

As previously noted, Chile is the largest producer of iodine, which is obtained as a by-product of the nitrate industry. Caliche, the crude, nitrate-bearing earth, contains $\frac{1}{2}$ to 1 pound of iodine per ton. The iodine, which is in the form of soluble sodium iodate, is released from the calcium along with the sodium nitrate. A certain amount of iodine is carried into commercial nitrate, but most of it is pregressively concentrated in the mother liquor remaining after the nitrate is crystallized out. The final mother liquor which contains about 8 grams per liter of iodine is treated with sulphurous acid or sodium bisulphite, usually the latter, which liberates the iodine. The liberated iodine is insoluble in the solution, and the precipitate is removed by filtration. The filter press cakes may be sold as crude iodine or the product may be purified by sublimation.

The sodium bisulphite necessary for the process is prepared locally. Sulphur, another associate mineral in the nitrate deposits, is burned to sulphur dioxide, which is passed into a solution of soda ash which in turn is obtained locally by heating nitrate of soda with coal.

Several processes have been devised for treating kelp. In the Scottish process the ash is lixiviated in a manner very similar to that used in the extraction of black ash for soda manufacture. The filtered liquor when evaporated yields a rough or "kelp" salt containing about equal proportions of sodium sulphate and potassium chloride, the latter being recovered by fractional crystallization. First sodium sulphate, and then common salt, crystallizes; and by further evaporation, sodium carbonate, together with more salt and potassium chloride, separates. The mother liquor is treated with sulphuric acid to decompose alkali sulphides and sulphites, and sodium sulphate and a little sulphur are removed. The liquor is then heated with manganese dioxide and strong sulphuric acid, thereby liberating iodine, which is recovered and then purified by sublimation. The pyrolusite is added in small doses periodically as long as iodine is given off; an excess liberates first bromine and then chlorine and causes loss of iodine, due to the formation of tribrom or trichlor iodine (ICl_3).

In the French process the iodine is precipitated (as cuprous iodide) from the clear liquid by means of copper sulphate in the presence of a reducing agent.

An important factor in the cost of extracting iodine and other chemicals from seaweed is the fuel cost for drying the weed before carbonization, and attempts have been made to avoid this by treating the wet weed directly. Two of such processes appear to have been successful. In the Devillers process, operated by the Societe Industrielle de l'Algue Marine, the weed is washed with fresh water, which extracts about 80 per cent of the iodine. The second direct process, elaborated by the Hercules Powder Co., involves fermentation of the weed. The latter process was used during the war. The raw material was the giant weed which grows along the Pacific coast and which was harvested by special boats. After being cut up on boards into small pieces, a slurry of weed and water was pumped into large tanks at the plant. After being inoculated with tertiary cultures of a suitable bacterium the mixture was allowed to ferment for a period of two weeks. The tanks contained about 50,000 gallons of material, and the gradually increasing amounts of acid formed during fermentation were neutralized by periodic additions of lime. At the end of the period the solid matter had almost completely gone into solution, and the filtered and neutralized liquid could be evaporated in Kestner quadruple-effect evaporators. The obvious disadvantage of the process is the cost of evaporation, the enormous plant required, and the comparative slowness of the fermentation operation. It is very doubtful if the present price of iodine would make the process an economic possibility.

The most important iodine compound is the potassium salt. This is made in several ways:[23]

(a) Iodine may be dissolved in caustic potash or carbonate solution, the solution evaporated to dryness, and the mixture of iodide and iodate so obtained calcined with powdered charcoal. The calcined mass is lixiviated and the potassium iodide crystallized out of the filtered solution;

(b) Since the foregoing method calls for very pure materials, a better method is to form ferroso-ferric iodide (Fe_3I_8) and then to decompose this salt with pure potassium carbonate. Metallic iron is dissolved by digesting it in a mixture of iodine and water, forming ferrous iodide, which is then treated with sufficient iodine to form the ferroso-ferric salt.

(c) Barium iodide is made by agitating barium sulphide solution with iodine, filtering, and boiling with potassium sulphate solution. The precipitated barium sulphate is filtered off, and the potassium iodide is obtained by evaporating the solution.

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[23] Thorp, F. H., Outlines of Industrial Chemistry: New York, 1916, pp. 254-5.

World Production

The output of iodine is determined by world demand and has increased rather slowly. In recent years the marketed production has frequently not exceeded 1,000 tons annually and this is only about three times the quantity sold in 1887 (319 tons).[24] A considerable part of this increase, however, has taken place within the last 15 or 20 years. Immediately before the outbreak of the World War, production averaged about 500 tons; in 1915, it reached a maximum of 1,500 tons; and following the Armistice it eventually adjusted itself to the present average, which is rather over than under 1,000 short tons.

Although production statistics are not quite complete it appears that Japan and France compete for second place among producing countries. Java, Great Britain, and more recently Norway are the only other producers of consequence at present. Available figures for recent years are given in the following table:

World Production of Iodine and Chilean Exports, 1916-1928[1]

(In metric tons)

Year	Chile Exports	Chile	Great Britain	France	Norway	Japan	Java	Total
1916	1,323	1,381	36	18	(2)	151	(2)	1,586
1917	759	734	45	31	(2)	122	(2)	932
1918	908	907	22	26	(2)	119	(2)	1,074
1919	505	429	24	65	(2)	83	(2)	601
1920	350	385	37	45	(2)	75	(2)	542
1921	534	488	32	39	(2)	60	(2)	619
1922	245	281	29	30	4	55	(2)	399
1923	471	462	36	61	4	59	36	658
1924	591	545	47	54	4	51	38	739
1925	569	786	25	55	5	49	56	
1926	1,132	906	(2)	(2)	(2)	[3] 63	67	
1927	871	779	(2)	(2)	(2)	[3] 64	65	
1928	788	995	(2)	(2)	(2)	[3] 53	74	

1 For 1916-1924 data are from Association of Iodine Producers, Chile. Through Mineral Industry, 1928, p. 70. Later figures from official publications.

2 Data not available.

3 Includes iodine content (calculated) of potassium iodide.

Domestic Production

Except during the World War the United States has produced little crude iodine. Virtually the entire domestic consumption of resublimed iodine and iodine compounds has been manufactured in this country from the imported crude product. In 1917 and 1918 a small quantity of iodine was obtained on the Pacific coast as a by-product of the manufacture of potash salts and acetone from kelp. These plants were erected to supply the large demand for acetone for military purposes and have since been closed. In 1918, according to the Geological Survey, there was produced in the United States 521,678 pounds of potassium iodide, from imported iodine. This output was from eight manufacturers. Quite recently (about 1929) however, the General Salt Co. in California (near Los Angeles) and the Dow Chemical Co. in Louisiana (near Shreveport) have succeeded in extracting iodine on a commercial scale from oil well waters. Since such waters must be de-oiled anyway in certain localities a certain amount of iodine can thus be obtained strictly as a by-product.

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[24] Thorpe, Edward, Dictionary of Applied Chemistry: London, vol. III, p. 647, 1922.

Census figures for the production of resublimed iodine and iodides for recent years are given in the following table:

Year	Resublimed iodine		Sodium and Potassium iodides	
	Pounds	Value	Pounds	Value
1923	97,070	$440,487	484,142	$1,812,839
1925	79,872	372,988	1/ 549,091	2,033,199
1927	- - -	- - -	575,999	2,105,456
1928	3	15	4	16
1929	- - -	- - -	2/ 1,262	5,181

1 Includes ammonium iodide.
2 Potassium iodide.

Imports

The consumption of iodine in the United States is mainly imported, largely from Chile, although occasional shipments have been made from Japan. The imports have been almost entirely of crude iodine, the purification by resublimation being carried out in this country. Considerable variation in the imports may be observed from year to year, indicating a tendency to maintain stocks in this country.

The imports of resublimed iodine have been virtually negligible, reaching a maximum of 15,550 pounds in 1918.

Iodine Imported for Consumption, 1918-1928

Year	Crude		Resublimed	
	Pounds	Value	Pounds	Value
1918	391,783	793,719	15,550	49,583
1919	1,251,086	2,385,226	2,925	10,743
1920	291,171	547,679	2,770	9,453
1921	644,711	1,425,934	1,500	4,730
1922	352,557	1,024,609	- - -	- - -
1923	273,338	883,361	24	45
1924	- - -	- - -	- - -	- - -
1925	246,474	889,860	1	6
1926	711,291	2,272,343	- - -	- - -
1927	926,492	2,900,574	- - -	- - -
1928	720,766	2,429,076	3	15
1929	627,162	2,249,266	- - -	- - -

Tariff Duties

Crude iodine was mentioned on the free list of the Act of 1883 and has been free of duty under all subsequent tariff acts, including the Act of 1930. Resublimed iodine, on the other hand, though free under the Acts of 1894 and 1913, has generally been dutiable. The rate under the Act of 1930 (par. 44) is 10 cents a pound, as compared with 20 cents under the Act of 1922. Potassium iodide is specifically mentioned under paragraph 73 of the present act, being dutiable at 25 cents a pound. Other iodine salts are dutiable under the blanket clause for chemical compounds not specially provided for (paragraph 5) at 25 per cent ad valorem.

Chile

Chile contributes about 90 per cent of the total world production of iodine. In 1928, 995 metric tons of iodine were produced, of which 788 metric tons, valued at $8,041,000, were exported. The United States took approximately half of these exports; and Germany, Great Britain, Russia, and Italy were the next best markets. It has been estimated that production in 1929 amounted to 1,387 metric tons.

During recent years the Chilean iodine industry has been reorganized to provide for active government supervision and the right to declare a government monopoly of iodine at any time. Even during the period when the monopolistic features of the Chilean nitrate industry broke down there was no apparent effect on the iodine monopoly.

The provinces of Tarapaca and Antofagasta contain practically all of the rich nitrate deposits of Chile. The nitrate-bearing material, known as "caliche," occurs in scattered deposits of both districts, ranging in thickness from 3 to 45 feet, averaging perhaps 15 feet. The iodine content in "caliche" ranges from 0.02 to 1 per cent. The average is close to 0.06 per cent or over 1 pound per ton, but because of the lack of a market only a fraction of the possible total is recovered. The estimated cost of the equipment for recovering iodine is about $65,000, and a number of the plants have not installed the necessary facilities for producing iodine and due to the impossibility of marketing more than a specified quota of iodine probably none of the plants produce more than a fraction of the quantity they could make if the consumption were less limited. The source of iodine is the mother liquor from the nitrate of soda operations; and the liquor after the iodates have been extracted may be used again for leaching the nitrate, but otherwise the production of iodine is wholly independent and distinct from the manufacture of nitrate of soda, and the iodine section of any of the Chilean works can be shut down without interrupting the regular nitrate operations

Other Foreign Countries

France.- The French iodine industry, located in Brittany, largely in the department of Finistere, depends almost entirely upon the local seaweed as a source of the raw material. Production is carried on in a very rudimentary manner. Under the methods in use at present 25 tons of seaweed or 5 tons of dried weed are required to produce 1 ton of ash, which yields approximately 10 kilos of iodine. The algin content is usually entirely lost.

Numerous small companies are producing, and it is therefore difficult accurately to estimate production. However, it is believed that the average production during the past few years has been 80 to 90 metric tons of crude iodine. About 15,000 workers are employed in the industry during the season of gathering the seaweed.

The French foreign trade in iodine is insignificant and variable. Crude iodine is imported in small quantities (2.6 metric tons in 1928) and exported in even smaller amounts (0.7 metric tons in 1928). There are no refined iodine imports, although small and varying quantities are exported (ranging from 2.6 metric tons in 1926 to 42.0 metric tons in 1928).

The sale of the iodine manufactured in Brittany is handled largely by two companies, one of which has formed a sort of comptoir of a large number of the manufacturers to handle the sale of their product; and another has a factory at Saint-Nazaire. This latter company is cooperative and sells only to members, who are usually druggists. In addition to these concerns, certain companies are engaged in treating crude and refined iodine.

Italy.- There are only five producers of iodine in Italy. Of these only two make crude iodine, and this in comparatively small quantities. Italian producers of crude iodine are the Soc. Anon. Regie Terme di Salsomaggioure, Salsomaggioure, and the Institute Chimico-Farmaceutico Militare, Turin, the former deriving the iodine from the mother liquors of the salso-bromo-iodic mineral water of Salsomaggioure, and the latter recovering the iodine from the waste water of the sterilization baths of the Institute.

Production of crude iodine is small. Statistics show that Italy also imports crude iodine which is then refined for the pharmaceutical trade. No crude iodine is exported, while exports of refined iodine are negligible, having amounted to 1,543 pounds in 1928 and nothing in 1929.

Until quite recently Italy has imported all its iodine requirements, to the value of 9.5 million lire annually. For the past two years experiments have been carried out, and brought to a successful conclusion, on the extraction of iodine from the waters of certain wells at Salsomaggioure. The water is pumped from a depth of 400 to 700 meters and contains 0.55 per cent of iodine, in addition to chlorides, bromides and sulphates of sodium, magnesium and lithium to the extent of 200 grams per liter. The water is treated with an oxidizing agent to liberate the iodine, which is extracted by petroleum on the countercurrent system. The iodine is removed chemically from the petroleum and reprecipitated. On an experimental plant producing 10 kg. of iodine per day, a 90 per cent yield was obtained.

The waters are owned by the State, which has just put down an extraction plant capable of supplying the whole of the domestic requirements of the country.

Japan.- Iodine is produced in Japan from kelp. During the war the output increased greatly but in recent years it has fallen off again.

Official statistics for the production of iodine in Japan are not available for later than the year 1927, but the following figures furnished by the Nihon Iodine Kabushiki Kaisha, considered to produce 95 per cent of the total production in Japan, are believed to be reliable: 1927 - 140 short tons; 1928 - 125 short tons; 1929 - 115 short tons; 1930 (estimated production) 240 short tons.[25]

Java.- Iodine is obtained in Java from the waters of springs and artesian wells, principally in the Soerebaya Residency. The yearly production in terms of pure iodine was formerly only 20 or 30 metric tons, but in 1925 it increased to 56 and in 1928 to 74 metric tons. The product is marketed in the form of cuprous iodide which is exported to England, the Netherlands, and Germany.

Norway.- A reliable source reports that efforts are being made to organize a new company for the manufacture of iodine from seaweed. The factory is to be located on the west coast of Norway, where seaweed is found in sufficiently large quantities to make the gathering profitable. It is now being done on a small scale. However, at present the iodine-containing ash obtained by burning the weed is being shipped to England for conversion into the finished product. The object of the promoters of the new company is to encourage the gathering of the raw material in larger quantities than is being done now.

Russia.- According to a Soviet Government statement[26] the Council of Labor and Defense has instructed the Gosmedtorgprom (State Medical Industry) to organize the production of iodine on a national basis. The work of constructing plants and stations for the treatment of seaweed has already been started in the north and far east and by the end of 1930 "a large quantity of iodine" was expected to be produced. Seaweed gathered from the White Sea will be treated in a plant to be constructed in that region, and investigations were under way for another enterprise utilizing seaweed from the shores of Murmansk. In the Archangel district subterranean waters containing iodine in the unusually high concentration of 50 milligrams per liter have been reported.

Markets and Prices

No definite statements have been issued by producers with regard to cost of production, but plant costs are generally assumed to have averaged recently around 30 to 35 cents (U. S. currency) per pound of crude iodine and if need arose this figure could undoubtedly be reduced to 25 cents a pound or less. The Chilean Government collects an export tax of 6 pesos per kilogram or approximately the equivalent of 32½ cents a pound. Adding shipping charges, insurance, etc., the cost laid down in New York City is probably under 70 cents a pound.

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[25] Asst. Trade Commissioner H. B. Titus, Tokyo. World Trade Notes, Dept. of Commerce, vol. 4, No. 18, p. 9, May 5, 1930.

[26] Soviet Union, Economic Review: June 15, 1930, pp. 265-266.

Quotations for crude iodine have not been regularly reported in trade journals. They are fixed in Chile by the Iodine Producers Association; and since the war they have remained in the neighborhood of $3.50 per pound, exclusive of the export duty.

The Iodine Association dominates the world market and was formed originally in 1878. In 1923 it became a part of the Nitrate Producers Association, but when the Nitrate Association, due to competition from synthetic nitrate, disintegrated in 1927, the Iodine Association still continued to function. Each plant is given a quota to produce each year, based upon its capacity to produce nitrate of soda. Often a plant would produce in one year enough for several years' needs and in such case is often able to borrow money from the banks, using the stored iodine as collateral. As a result of this procedure many banks in Chile are deeply interested in sustaining prices. The Chilean monopoly has an agreement with the Scottish and French producers as regards distribution and sales, but it is believed that the Japanese and Javanese producers have not joined the international cartel. A further function of the Chilean association is to carry on propaganda with a view to increasing the use of iodine.

Due to lack of fluctuations in the price of crude iodine the quotations for resublimed iodine and the leading compounds have been quite steady for a number of years. In July, 1930, the following quotations appeared in the Oil, Paint, and Drug Reporter:

	Per pound
Iodine, resublimed, kegs	$4.65 - 4.70
Sodium iodide, jars	4.25 - 4.30
Potassium iodide, barrels, fiber drums	3.25 - 3.30
Ammonium iodide, jars	5.20
Iodoform, kegs	6.50 - 6.55

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